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**WO 02/48293 A1**

(54) Title: **ULTRA-LOW SULFUR FUEL COMPOSITIONS CONTAINING ORGANOMETALLIC ADDITIVES**

(57) Abstract: A method, apparatus, and fuel composition for the protection of a catalytic after treatment system and a method for protecting a catalytic after treatment system in a low sulfur fuel system are disclosed. A scavenging agent is introduced into the base fuel in an amount effective to complex with catalytic poisoning combustion by products and reduce catalyst poisoning. In a preferred embodiment, the scavenger is an organometallic compound which also imparts additional desirable properties to the fuel.

## ULTRA-LOW SULFUR FUEL COMPOSITIONS CONTAINING ORGANOMETALLIC ADDITIVES

### BACKGROUND OF THE INVENTION

#### 5      **Field of the Invention**

The present invention relates, generally, to ultra-low sulfur fuel compositions containing organometallic additives and a method of protecting emissions systems. Emissions systems as used herein broadly includes catalysts and associated equipment which is generally located in the effluent stream of a combustion system, e.g. in the 10 exhaust or the like. The invention contemplates the addition of various compounds to an ultra low sulfur fuel to protect the emissions systems from poisoning by exhaust byproducts, and a method of protecting emissions systems from poisoning from impurities found in the fuel and lubricant sources and increasing the catalyst durability in these systems.

15      More specifically, the present invention relates to ultra-low sulfur fuel compositions containing an organometallic compound which acts as a scavenger to prevent poisoning deposits such as sulfur, phosphorus or lead on catalytic emissions systems used for reducing tailpipe emissions, thereby contributing to lowered emissions characteristics and improved emissions system efficiency, thereby contributing to 20 lowered emissions characteristics and improved emissions system efficiency and improved emission hardware (e.g., catalyst) durability.

#### **Description of the Prior Art**

It is well known in the automobile industry to reduce tailpipe emissions by using various strategies. The most common method for reducing emissions from spark ignition

engines is by careful control of the air-fuel ratio and ignition timing. For example, retarding ignition timing from the best efficiency setting reduces HC and NO<sub>x</sub> emissions, while excessive retard of ignition increases the output of CO and HC. Increasing engine speed reduces HC emissions, but NO<sub>x</sub> emissions increase with load. Increasing coolant 5 temperature tends to reduce HC emissions, but this results in an increase in NO<sub>x</sub> emissions.

It is also known that treating the effluent stream from a combustion process by exhaust after treatment can lower emissions. The effluent contains a wide variety of chemical species and compounds, some of which may be converted by a catalyst into 10 other compounds or species. For example, it is known to provide exhaust after treatment including a three-way catalyst and a lean NO<sub>x</sub> trap. Other catalytic and non-catalytic methods are also known.

Thermal reactors are noncatalytic devices which rely on homogeneous bulk gas reactions to oxidize CO and HC. However, in thermal reactors, NO<sub>x</sub> is largely 15 unaffected. Reactions are enhanced by increasing exhaust temperature (e.g. by a reduced compression ratio or retarded timing) or by increasing exhaust combustibles (rich mixtures). Typically, temperatures of 1500 °F (800 °C) or more are required for peak efficiency. Usually, the engine is run rich to give 1 percent CO and air is injected into the exhaust. Thermal reactors are seldom used, as the required setting dramatically reduces 20 fuel efficiency.

Catalytic systems are capable of reducing NO<sub>x</sub> as well as oxidizing CO and HC. However, a reducing environment for NO<sub>x</sub> treatment is required which necessitates a richer than chemically correct engine air-fuel ratio. A two-bed converter may be used in

which air is injected into the second stage to oxidize CO and HC. While efficient, this procedure results in lower fuel economy.

Single stage, three way catalysts (TWC's) are widely used, but they require extremely precise fuel control to be effective. Only in the close proximity of the  
5 stoichiometric ratio is the efficiency high for all three pollutants, excursions to either side of stoichiometric can cause increase in hydrocarbon and carbon monoxide or NO<sub>x</sub> emissions. Such TWC systems can employ, for example, either a zirconia or titanium oxide exhaust oxygen sensor or other type of exhaust sensor and a feedback electronic controls system to maintain the required air-fuel ratio near stoichiometric.

10 Catalyst support beds may be pellet or honeycomb (e.g. monolithic). Suitable reducing materials include ruthenium and rhodium, while oxidizing materials include cerium, platinum and palladium.

Diesel systems raise a different set of challenges for emissions control. Strategies for reducing particulate and HC include optimizing fuel injection and air motion,  
15 effective fuel atomization at varying loads, control of timing of fuel injection, minimization of parasitic losses in combustion chambers, low sac volume or valve cover orifice nozzles for direct injection, reducing lubrication oil contributions, and rapid engine warm-up.

In terms of after treatment, it is known that diesel engines generally burn lean and  
20 the exhaust will therefore usually contain excess oxygen. Thus, NO<sub>x</sub> reduction with conventional three-way catalysts is not feasible. NO<sub>x</sub> is removed from diesel exhaust by either selective catalytic reduction, the use of lean NO<sub>x</sub> catalysts such as those comprised

of zeolitic catalysts or using metals such as iridium, or catalyzed thermal decomposition of NO into O<sub>2</sub> and N<sub>2</sub>.

Diesel particulate traps have been developed which employ ceramic or metal filters. Thermal and catalytic regeneration can burn out the material stored. Particulate 5 standards of 0.2 g/mile may necessitate such traps. Both fuel sulfur and aromatic content contribute to particulate emissions. Catalysts have been developed for diesels which are very effective in oxidizing the organic portion of the particulate.

Improved fuel economy can be obtained by using a lean-burn gasoline engine, for example, a direct injection gasoline engine, however currently NO<sub>x</sub> cannot be reduced 10 effectively from oxidizing exhaust using a typical three-way catalyst because the high levels of oxygen suppress the necessary reducing reactions. Without a NO<sub>x</sub> adsorber or lean NO<sub>x</sub> trap (LNT), the superior fuel economy of the lean-burn gasoline engine cannot be exploited. The function of the LNT is to scavenge the NO<sub>x</sub> from the exhaust, retaining 15 it for reduction at some later time. Periodically, the LNT must be regenerated by reducing the NO<sub>x</sub>. This can be accomplished by operating the engine under rich air-fuel ratios for the purpose of purging the trap. This change in operating conditions can adversely effect fuel economy as well as driveability. These LNT's may also be placed on diesel engines, which also operate in a lean air-fuel mode. As in the lean-burn gasoline engines, the 20 exhaust of both types of engines is net oxidizing and therefore is not conducive to the reducing reactions necessary to remove NO<sub>x</sub>. It is an object of the present invention to improve the storage efficiency and durability of the LNT and to prolong the useful life of the LNT before regeneration is necessary.

It is well known that NO<sub>x</sub> adsorbers are highly vulnerable to deactivation by sulfur (see, for example, M. Guyon et al., *Impact of Sulfur on NO<sub>x</sub> Trap Catalyst Activity-Study of the Regeneration Conditions*, SAE Paper No. 982607 (1998); and P. Eastwood, *Critical Topics in Exhaust Gas Aftertreatment*, Research Studies Press Ltd. (2000) 5 pp.215-218.) and other products resulting from fuel combustion and normal lubricant consumption. The US Environmental Protection Agency (EPA) has set forth proposed rules for limiting the sulfur content of highway diesel fuels to a level of 15 parts per million (see 65 FR 35429, June 2, 2000, the complete text of which is incorporated herein by reference). The EPA states "This proposed sulfur standard is based on our assessment 10 of how sulfur-intolerant advanced exhaust emission control technologies will be." It is an object of the present invention to provide fuel or lubricant compositions capable of reducing the adverse impact of sulfur, and other exhaust byproducts, on catalytic emissions control technologies including NO<sub>x</sub> adsorbers and LNTs. Further, the present invention provides refiners with flexibility in complying with the objective of said 15 proposed rule by allowing refiners to reduce sulfur to a certain level above the 15 ppm level of the rule and still obtain the benefits of improved exhaust emissions control technology performance obtained by using fuels containing lower levels of sulfur.

Performance fuels for varied applications and engine requirements are known for controlling combustion chamber and intake valve deposits, cleaning port fuel injectors 20 and carburetors, protecting against wear and oxidation, improving lubricity and emissions performance, and ensuring storage stability and cold weather flow. Fuel detergents, dispersants, corrosion inhibitors, stabilizers, oxidation preventers, and performance additives are known to increase desirable properties of fuels.

Organometallic manganese compounds, for example methylcyclopentadienyl manganese tricarbonyl (MMT), available from Ethyl Corporation of Richmond, Virginia, is known for use in gasoline as an antiknock agent (see, e.g. US Patent 2,818,417). These manganese compounds have been used to lower deposit formation in fuel induction systems (US Patents 5,551,957 and 5,679,116), sparkplugs (US Patent 4,674,447) and in exhaust systems (US Patents 4,175,927, 4,266,946, 4,317,657, and 4,390345). Organometallic iron compounds, such as ferrocene, are known as well for octane enhancement (US Patent 4,139,349).

## 10 SUMMARY OF THE INVENTION

The present invention contemplates supplying, in a spark- or compression ignition lean, stoichiometric, or rich system, a low sulfur fuel containing a sufficient amount of an organometallic compound, e.g. MMT or the like, to effectively reduce the impact of poisoning substances on emissions systems for fuel-combustion systems.

15 The combustion of a fuel containing an organometallic manganese compound, such as MMT, results in mixtures of manganese compounds containing, among others, species of manganese oxides, manganese phosphates and manganese sulfates. As used hereinafter, a stoichiometric ratio will be referred to using lambda, which is calculated using the following formula:

20 
$$\lambda = \frac{\text{air /fuel ratio}}{\text{stoichiometric air/fuel ratio.}}$$

When  $\lambda = 1$ , the system is stoichiometric. When  $\lambda > 1$ , or more preferably  $> 1.02$ , the system is a lean system. When  $\lambda < 1$ , the system is a rich system.

In a gasoline or diesel engine that is operating with excess air according to the present invention, under lean conditions and using a fuel containing an organometallic compound according to the present invention, the metal will combine with combustion byproducts, e.g. sulfur, to form, e.g., metal sulfates in the exhaust. These compounds are 5 not stable at the high temperatures found in the exhaust manifold or those associated around typical three way catalysts. However, at lower temperatures under which lean NO<sub>x</sub> catalysts, diesel particulate traps, continuously regenerating traps, lean NO<sub>x</sub> traps or diesel oxidation catalysts operate, the metal can scavenge the sulfur and form stable metal sulfate compounds. This scavenging process then ties up the sulfur and protects the 10 catalyst from sulfur deposition. Suitable exhaust temperatures are below 650 °C, preferably below 600 °C and more preferably below about 500 °C. For example, from about 200 to about 650 °C.

Surprisingly, when a compound according to the present invention is used in a fuel containing low amounts of sulfur, the conversion efficiency of emissions systems is 15 maintained at a much higher rate than when the base fuel is used alone.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graphical representation comparing the sulfur content on a diesel oxidation catalyst aged 80,000 km on base diesel fuel (Base) or additized diesel fuel containing 20 organometallic compounds (Metal).

Figure 2 is a graphical representation comparing NO<sub>x</sub> conversion loss of a lean NO<sub>x</sub> trap with a spark-ignition base fuel and the base fuel plus an organometallic compound according to the present invention, wherein the base fuel contains 30 ppm sulfur.

Figure 3 is a graphical representation comparing NO<sub>x</sub> conversion of a lean NOx trap after operating 46 hours on a base fuel and a fuel composition according to the present invention.

Figure 4 is a graphical representation comparing NO<sub>x</sub> conversion loss of a catalysts with  
5 a spark-ignition base fuel and the base fuel plus an organometallic compound according  
to the present invention, wherein the base fuel contains 30 ppm sulfur.

#### DETAILED DESCRIPTION

Catalytic based emissions systems are well known. As exhaust emissions control  
10 systems become more advanced and emissions restrictions become tighter, the  
susceptibility of emissions control systems to poisoning increases.

Exhaust emission control systems have a tendency to lose their effectiveness over  
time. The present invention contemplates providing an organometallic compound to a  
low sulfur fuel composition. Suitable organometallic compounds include those  
15 containing at least one alkali, alkaline earth or transition metal in conjunction with an  
appropriate ligand.

The fuel compositions of the present invention can further enhance the emissions  
control system protection of the low sulfur fuel. Also, the present invention allows for  
use of fuels having a higher sulfur content to function in a similar manner to a fuel having  
20 a lower sulfur content with respect to protecting the exhaust emission control  
technologies.

Preferred metals include sodium, potassium, calcium, barium, strontium, rhodium,  
cerium, palladium, platinum, iron, manganese and mixtures thereof. The addition of a

variety of organometallic compounds to fuel compositions is known. Representative organometallic compounds for use in the present invention include those compounds taught in US Patents 4,036,605; 4,104,036; 4,474,580; 4,568,357; 4,588,416; 4,674,447; 4,891,050; 4,908,045; 4,946,609; 4,955,331; 5,113,803; 5,599,357; 5,919,276; 5 5,944,858; 6,051,040 and 6,056,792; and European Patent EP 466 512 B1.

Especially preferred organometallic compounds are those containing at least one of the metals selected from the group consisting of manganese, iron, strontium, cerium, barium, platinum and palladium. Preferred manganese containing organometallic compound are manganese tricarbonyl compounds delivered in the fuel or through the 10 lubricating composition. Such compounds are taught, for example, in US Patent Nos. 4,568,357; 4,674,447; 5,113,803; 5,599,357; 5,944,858 and European Patent No. 466 512 B1. Other methods of delivery, including direct injection into the combustion chamber or exhaust, are also suitable for practice of the instant invention.

Suitable manganese tricarbonyl compounds which can be used in the practice of 15 this invention include cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, dimethylcyclopentadienyl manganese tricarbonyl, trimethylcyclopentadienyl manganese tricarbonyl, tetramethylcyclopentadienyl manganese tricarbonyl, pentamethylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, diethylcyclopentadienyl manganese 20 tricarbonyl, propylcyclopentadienyl manganese tricarbonyl, isopropylcyclopentadienyl manganese tricarbonyl, tert-butylcyclopentadienyl manganese tricarbonyl, octylcyclopentadienyl manganese tricarbonyl, dodecylcyclopentadienyl manganese tricarbonyl, ethylmethylcyclopentadienyl manganese tricarbonyl, indenyl manganese

tricarbonyl, and the like, including mixtures of two or more such compounds. Preferred are the manganese tricarbonyl compounds which are liquid at room temperature such as methylcyclopentadienylmanganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, liquid mixtures of cyclopentadienyl manganese tricarbonyl and 5 methylcyclopentadienyl manganese tricarbonyl, mixtures of methylcyclopentadienyl manganese tricarbonyl and ethylcyclopentadienyl manganese tricarbonyl, etc.

Preparation of such compounds is described in the literature, for example, U.S. Pat. No. 2,818,417, the disclosure of which is incorporated herein in its entirety.

When formulating fuel compositions of this invention, the organometallic 10 compounds (e.g., cyclopentadienyl manganese tricarbonyl compounds) are employed in amounts sufficient to reduce the impact of poisons, e.g., sulfur, lead and phosphorus, on the emissions systems of a low sulfur fuel fired engine. Thus the fuels will contain minor amounts of the organometallic compounds sufficient to control the impact of such deposits on catalytic exhaust emission control technologies. Generally speaking, the 15 fuels of the invention will contain an amount of the organometallic compound sufficient to provide from about 0.5 to about 120 mg of metal per liter of fuel, and preferably from about 1 to about 66 mg of manganese per liter and more preferably from about 2 to about 33 mg of metal per liter of fuel. When added to the lubrication systems of automobiles as a means of delivering the metal to the fuel combustion system, the organometallic 20 concentration will be increased to provide the above amounts of the metal in the combustion chamber.

While not wishing to be bound by the following theory, it is postulated that the sulfur in the fuel reacts with the metal, for example the manganese in MMT, to form

metal sulfate ( $M\text{SO}_4$ ) which are stable in the temperature range of 200-650 °C.

Surprisingly, metal sulfates such as  $\text{MnSO}_4$  do not bind to active sites on the catalyst whereas free sulfur does, in the form of a sulfate.

When the emissions system contains a component (e.g. a barium-containing lean

5     $\text{NO}_x$  trap) which is poisonable by combustion products, applicants novel compositions and methods provide a substance which competes with the active site (e.g. barium) in the low-sulfur fueled engine-out exhaust. So long as the metal of the scavenging agent will compete with the metal of the catalyst system for complexing with the sulfur, the metals may be suitable for use as scavenging agents in the practice of the present invention. The  
10    ability of the metal scavenging agent to compete with the metals of the catalyst for complexing with the catalyst poisons can be determined by monitoring catalyst durability. Further, the organometallic scavengers of the present invention can reduce the detrimental impact of other poisons, such as phosphorus and lead, on emissions control technologies of the combustion systems of the present invention.

15       It is especially preferred that the sulfur content of the fuel be less than 100 ppm, and the treatment rate of the organometallic compound be up to 120 mg/l, more preferably up to 66 mg/l, and most preferably up to 33 mg/l, based upon the amount of metal delivered to the fuel composition. Higher rates are possible, but excessive treatment of the fuel stock may be detrimental to proper functioning of the combustion  
20    system componentry.

In a combustion engine, normal operation results in the combustion of the lubricant and additives such as those containing phosphorus or zinc added to the lubricant. In addition to the sulfur present in the fuel, the compositions of the present

invention interact with the combustion products of these additives and reduce their adverse impact on exhaust aftertreatment devices. By preventing deposition, the novel compositions prevent the compounds, such as phosphorus, from covering catalyst or storage sites in the aftertreatment systems and reducing the aftertreatment system's

- 5 effectiveness. With the compositions of the present invention, the aftertreatment system's effectiveness is maintained over extended periods of operation.

### Examples

#### Example 1

- 10 Two vehicles equipped with diesel engines and oxidation catalysts were tested over 80,000 km. One vehicle used diesel fuel. The other used diesel fuel containing organometallic additives in an amount sufficient to provide 17 ppm calcium and 3 ppm manganese to the fuel. At the end of mileage accumulation the two catalysts were removed from the vehicle and the elemental content of these catalysts was evaluated. As  
15 seen in Figure 1, the catalysts from the vehicle operated on a fuel containing organometallic scavengers contained lower amounts of sulfur. This demonstrates that use of organometallic compounds scavenges sulfur and prevents its deposition on the catalyst.

#### Example 2.

- These same diesel catalysts were examined for other catalyst poisons as shown in  
20 Table 1 below. The catalyst from the engine operated according to the present invention was found to contain lower amounts of phosphorus and lead compared to the catalysts from the vehicle using base fuel. This scavenging of P and Pb has not been observed in engines that run significantly greater air than stoichiometric or in diesel engine

applications. The presence of P and Pb on a catalyst would reduce catalyst activity; therefore, the scavenging of these compounds by the additive should provide greater catalyst durability.

5 TABLE I - CATALYST POISON CONTENT (ppm)

	Base Fuel Catalysts	Pb	P	S	MMT Fuel Catalysts	Pb	P	S	
Front in	22	4756	2344		Front in	19.6	1565	812	
	24	4375	2518			12.8	1294	331	
	out	20.9	4303	1812		out	16.6	1046	1586
10 Rear in	26	4246	2683		Rear in	16.1	1379	1623	
	mid	25	2094	2543		mid	17.8	944	1111
	out	23.8	1361	3098		out	17.8	794	965
Average		23.62	3522.5	2499.7	Average	16.78	1170.3	1071.33	

15 As may be seen from the above examples, the addition of the organometallic compound acts to reduce the deposits of P, Pb and S upon the catalyst structure, thereby enhancing life and maintaining efficiency of the emissions system and reducing overall emissions.

Such a reduction of deposits on catalysts is unexpected, as heretofore, such catalysts have been suitable only for so-called stoichiometrically balanced systems, and it is unexpected that an unbalanced system, e.g. a lean fuel combustion system, would work. It has been understood that for such three-way catalysts to work, they must be exactly matched to the stoichiometry of the combustion system or the production of

emissions would be above that which is achievable with the practice of the instant invention.

Further, the method according to the instant invention is especially useful in low sulfur fuels, e.g., those with less than 100 ppm, preferably 50 ppm or less, more

- 5 preferably 30 ppm or less, most preferably 20 ppm or less, for example 15 ppm or less, sulfur as it enhances the sulfur emissions reduction without the need to resort to more expensive desulfurization procedures.

An especially preferred sulfur range in the fuel according to the present invention is from about 20 to about 50 ppm sulfur. The deleterious effects of other catalyst poisons,

- 10 including those such as phosphorus and lead are also suitable for reduction according to the present invention by providing competing scavengers according to the present invention. Thus the advantages of the present invention can still be recognized with fuels containing ultra-low levels of sulfur, for example 15 ppm or less, 5 ppm or less as well as sulfur-free fuels.

- 15 The base fuels used in formulating the compositions of the present invention include base fuels suitable for use in the operation of spark-ignition or compression-ignition internal combustion engines such as diesel fuel, jet fuel, kerosene, unleaded motor and aviation gasolines, and so-called reformulated gasolines which typically contain both hydrocarbons of the gasoline boiling range and fuel-soluble oxygenated blending agents, such as alcohols, ethers and other suitable oxygen-containing organic compounds. Oxygenates suitable for use in the present invention include methanol, ethanol, isopropanol, t-butanol, mixed C<sub>1</sub> to C<sub>5</sub> alcohols, methyl tertiary butyl ether, tertiary amyl methyl ether, ethyl tertiary butyl ether and mixed ethers. Oxygenates, when

used, will normally be present in the base fuel in an amount below about 25% by volume, and preferably in an amount that provides an oxygen content in the overall fuel in the range of about 0.5 to about 5 percent by volume.

- In a preferred embodiment, the middle-distillate fuel is a diesel fuel having a
- 5     sulfur content of up to about 0.01%, preferably 0.005% or less, more preferably 0.003% or less, by weight, as determined by the test method specified in ASTM D 2622-98.

### Example 3

A commercial lean NO<sub>x</sub> trap from a direct injection gasoline (DIG) engine was cored and cut into 1 inch by  $\frac{3}{4}$  inch diameter samples. A catalyst sample was placed in a

10    1 inch stainless tube which in turn was in an electric oven down stream of a pulsed flame combustor. The pulsed flame combustor burned iso-octane with and without MMT. The combustor cycle was 5 min. consisting of 4 min. lean operation to trap NO<sub>x</sub> ( $\lambda$  1.3 with NO<sub>x</sub> added to give 500ppm to the catalyst), and 1 min. rich operation to reduce the trapped NO<sub>x</sub> ( $\lambda$  0.9 with no added NO<sub>x</sub>). Typically the catalyst approached

15    saturation with NO<sub>x</sub> at the end of the 4 min. lean period so NO<sub>x</sub> conversion were measured during the first 1 min. of the lean period to give data more representative of a commercial vehicle. The catalyst oven provided a constant catalyst temperature. SO<sub>2</sub> gas could be added to the combustor to simulate exhaust from a 30ppm sulfur fuel.

Turning now to Figures 2 and 3, experimental data from a lean NO<sub>x</sub> trap

20    evidences the beneficial properties of the present invention. The experimental protocol was as follows: exhaust gas from a 30 ppm sulfur equivalent fuel was run over the lean NO<sub>x</sub> catalysts for 46 hours with the catalyst temperature 350C. The NO<sub>x</sub> conversion was measured constantly throughout the test. The MMT fuel contained MMT at 18 mg

Mn/liter. Reported conversion was calculated for the first 1 minute at lean operation.

The loss in NO<sub>x</sub> conversion on an hourly basis is substantially higher for non-MMT containing fuels.

Figure 2 illustrates the deterioration rate for NO<sub>x</sub> conversion. Conversely, this

5 could be looked upon as the rate of sulfur poisoning of the conversion process. As can be seen from this data, MMT at 18 mg Mn/liter protected the catalyst from sulfur poisoning and resulted in a deterioration rate that was only 80% of that observed from base fuel without MMT.

Figure 3 illustrates the lean NO<sub>x</sub> Trap NO<sub>x</sub> efficiency at the end of test for several

10 temperatures. The LNT operated on a fuel containing MMT displayed higher activity across a range of temperatures.

Figure 4 illustrates the deterioration rate for NO<sub>x</sub> conversion with four separate catalyst samples from the same catalyst. Samples #1 and #2 utilized base fuel and samples #3 and #4 utilized a fuel containing MMT. Both samples with MMT showed 15 lower deterioration rates. Since the differences in deterioration rates are much greater than the 95% confidence limits, these differences are considered statistically significant.

The present invention is suitable for use in all combustion systems including burners and large and small engines, such as 4 stroke and 2 stroke engines, e.g. those in generators, leaf blowers, trimmers, snow blowers, marine engines, or other types of 20 engines which may have the scavenger delivered to the combustion chamber. The scavenger is effective in the effluent stream of an exhaust system, especially where the emissions control is downstream from the combustion system.

It is to be understood that the reactants and components referred to by chemical name anywhere in the specification or claims hereof, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (e.g., base fuel, solvent, etc.). It matters

- 5 not what chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution or reaction medium as such changes, transformations and/or reactions are the natural result of bringing the specified reactants and/or components together under the conditions called for pursuant to this disclosure. Thus the reactants and components are identified as ingredients to be brought together either in performing a
- 10 desired chemical reaction (such as formation of the organometallic compound) or in forming a desired composition (such as an additive concentrate or additized fuel blend). It will also be recognized that the additive components can be added or blended into or with the base fuels individually per se and/or as components used in forming preformed additive combinations and/or sub-combinations. Accordingly, even though the claims
- 15 hereinafter may refer to substances, components and/or ingredients in the present tense ("comprises", "is", etc.), the reference is to the substance, components or ingredient as it existed at the time just before it was first blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure.

The fact that the substance, components or ingredient may have lost its original identity

- 20 through a chemical reaction or transformation during the course of such blending or mixing operations is thus wholly immaterial for an accurate understanding and appreciation of this disclosure and the claims thereof.

At numerous places throughout this specification, reference has been made to a number of U.S. Patents and published foreign patent applications. All such cited documents are expressly incorporated in full into this disclosure as if fully set forth herein.

5 This invention is susceptible to considerable variation in its practice. Therefore the foregoing description is not intended to limit, and should not be construed as limiting, the invention to the particular exemplifications presented hereinabove. Rather, what is intended to be covered is as set forth in the ensuing claims and the equivalents thereof permitted as a matter of law.

10 Patentee does not intend to dedicate any disclosed embodiments to the public, and to the extent any disclosed modifications or alterations may not literally fall within the scope of the claims, they are considered to be part of the invention under the doctrine of equivalents.

Having described the invention as above, we claim:

1. A method of enhancing performance durability of a catalytic emissions control system in a fuel combustion system containing a catalytic device having a transition metal, alkali or alkaline earth metal element, or combinations thereof (catalytic elements), said combustion system producing at least one byproduct, comprising:

supplying a fuel containing 100 ppm or less sulfur to said fuel combustion system,  
said combustion system being provided with a scavenger, said scavenger  
complexing with at least one combustion byproduct,  
said scavenger being supplied in an effective amount to complex with the at least  
one fuel combustion byproduct,  
whereby the impact of said fuel combustion byproduct on said emissions control  
system are reduced.

2. The method of claim 1, wherein said fuel contains 50 ppm or less sulfur.

3. The method of claim 2, wherein said fuel contains 30 ppm or less sulfur.

4. The method of claim 3, wherein said fuel contains 20 ppm or less sulfur.

5. The method of claim 4, wherein said fuel contains 15 ppm or less sulfur.

6. The method of claim 1, wherein said fuel comprises a spark-ignition fuel.

7. The method of claim 1, wherein said fuel comprises a compression-ignition fuel.

8. A method as claimed in claim 1, wherein the scavenger is an organometallic compound.

9. A method as claimed in claim 8, wherein the scavenger includes at least one metal selected from the group consisting of magnesium, manganese, barium, cerium, strontium, iron, calcium, platinum, palladium and mixtures thereof.

10. A method as claimed in claim 8, wherein the scavenger comprises at least one alkali and/or alkaline earth metal.

11. A method as claimed in claim 8, wherein the scavenger comprises at least one transition metal.

12. A method as claimed in claim 11, wherein said organometallic compound at least one manganese tricarbonyl compound.

13. A method as claimed in claim 1, wherein the scavenger is present in an amount so as to provide from 0.5 to about 120 mg of metal per liter of fuel.

14. A method as claimed in claim 13, wherein the scavenger is present in an amount so as to provide from about 1 to about 66 mg of metal per liter of fuel.

15. A method as claimed in claim 1, wherein the combustion system operates at a lambda > 1.2.

16. A method as claimed in claim 1, wherein the emissions reduction system comprises a catalytic convertor.

17. A method as claimed in claim 1, wherein the emissions reduction system comprises a lean NO<sub>x</sub> trap.

18. A method as claimed in claim 1, wherein the catalytic device comprises barium.

19. An apparatus for reducing emissions control system poisoning in a lean fuel combustion system having a stream of effluent, comprising:

a combustion system which operates at a lambda > 1,

a base fuel containing 100 ppm or less sulfur, and

present, in an effective amount to complex with at least one combustion

byproduct in the effluent stream, a scavenger.

20. The apparatus of claim 19, wherein the base fuel contains 50 ppm or less sulfur.

21. An apparatus as claimed in claim 19, wherein the scavenger comprises at least one organometallic compound.

22. An apparatus as claimed in claim 21, wherein the organometallic compound comprises at least one manganese tricarbonyl compound.

23. An apparatus as claimed in claim 19, wherein the scavenger comprises at least one element selected from the group consisting of transition metal elements.

24. An apparatus as claimed in claim 19, wherein the scavenger comprises at least one metal selected from the group consisting of magnesium, manganese, barium, cerium, strontium, iron, calcium, platinum, palladium and mixtures thereof.

25. An apparatus as claimed in claim 19, wherein the fuel comprises a compression-ignition fuel and the emissions control system comprises at least one member selected from the group consisting of an oxidation catalyst, a three-way catalyst, a catalyzed particulate trap, exhaust gas sensors and a lean NO<sub>x</sub> trap.

26. An apparatus as claimed in claim 19, wherein the fuel comprises a spark-ignition fuel and the emissions control system comprises at least one member selected from the group consisting of an oxidation catalyst, a three-way catalyst, exhaust gas sensors and a lean NO<sub>x</sub> trap.

27. A catalytic emissions control system for the after treatment of a combustion process exhaust stream, comprising:

an exhaust passageway for the passage of an exhaust stream containing exhaust byproducts from the combustion of a fuel,  
at least one catalytic material having catalytic activity, said catalytic material being located within the exhaust passageway and contacting the exhaust stream,  
wherein the exhaust stream contains a scavenger which complexes with at least one of the exhaust byproducts and reduces the impact of the byproduct upon the catalytic material, and  
wherein said fuel contains 100 ppm or less sulfur.

28. An emissions system as claimed in claim 27, wherein the scavenger comprises an organometallic compound.

29. An emissions system as claimed in claim 27, wherein the scavenger comprises at least one manganese tricarbonyl compound.

30. An emissions system as claimed in claim 27, wherein the combustion exhaust byproducts comprises sulfur.

FIGURE 1

### Sulfur Content on Diesel Oxidation Catalyst

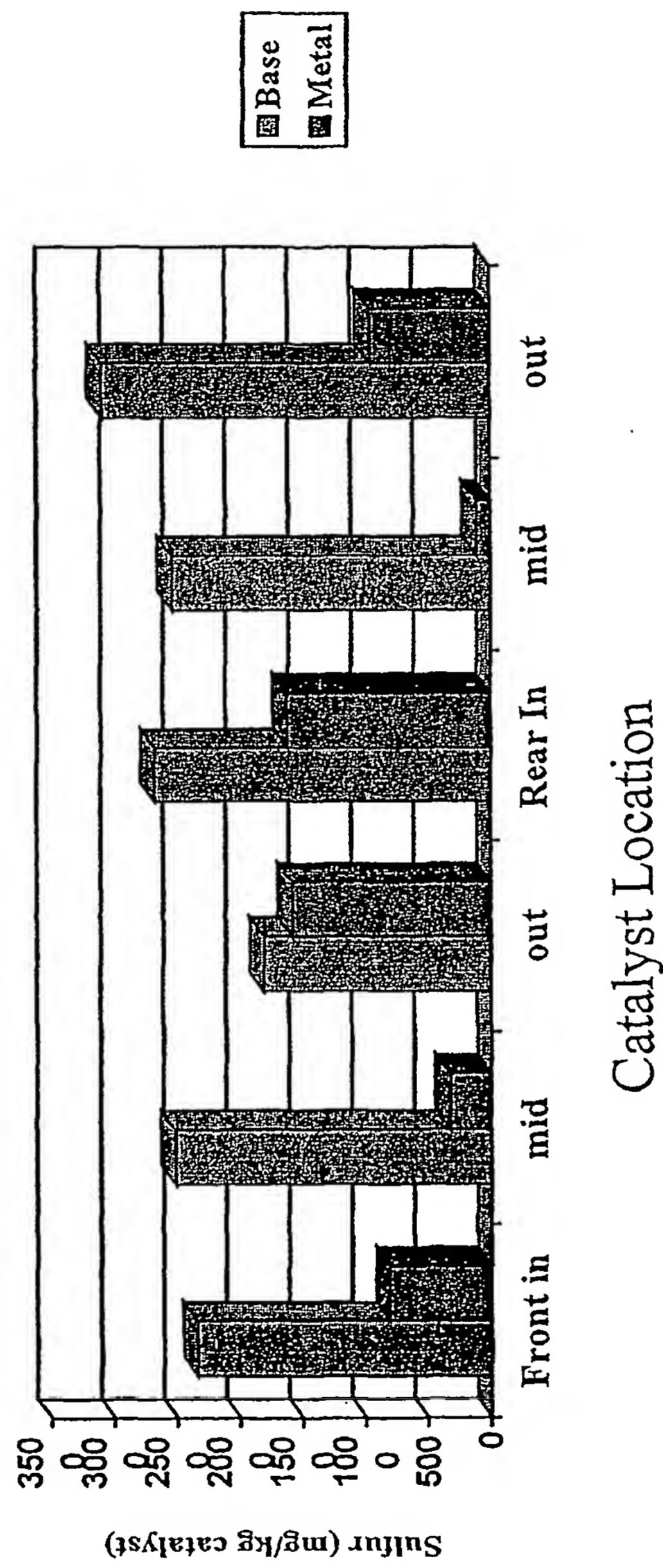


FIGURE 2

NO<sub>x</sub> Conversion Loss with Equivalent of  
30ppm Sulfur Fuel

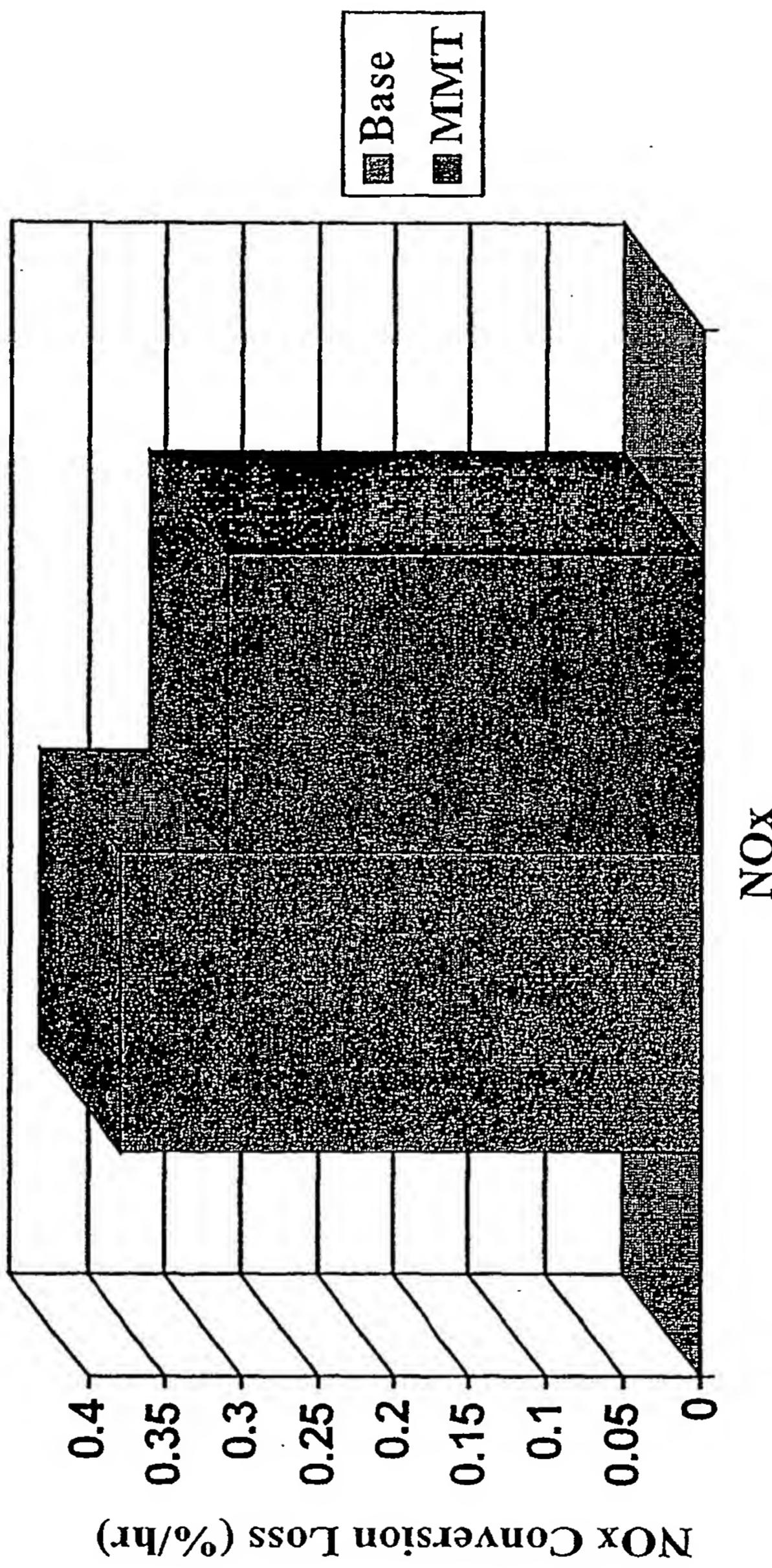


FIGURE 3  
NO<sub>x</sub> Conversion After Operating 46 Hours on  
Equivalent of 30 ppm Sulfur Fuel

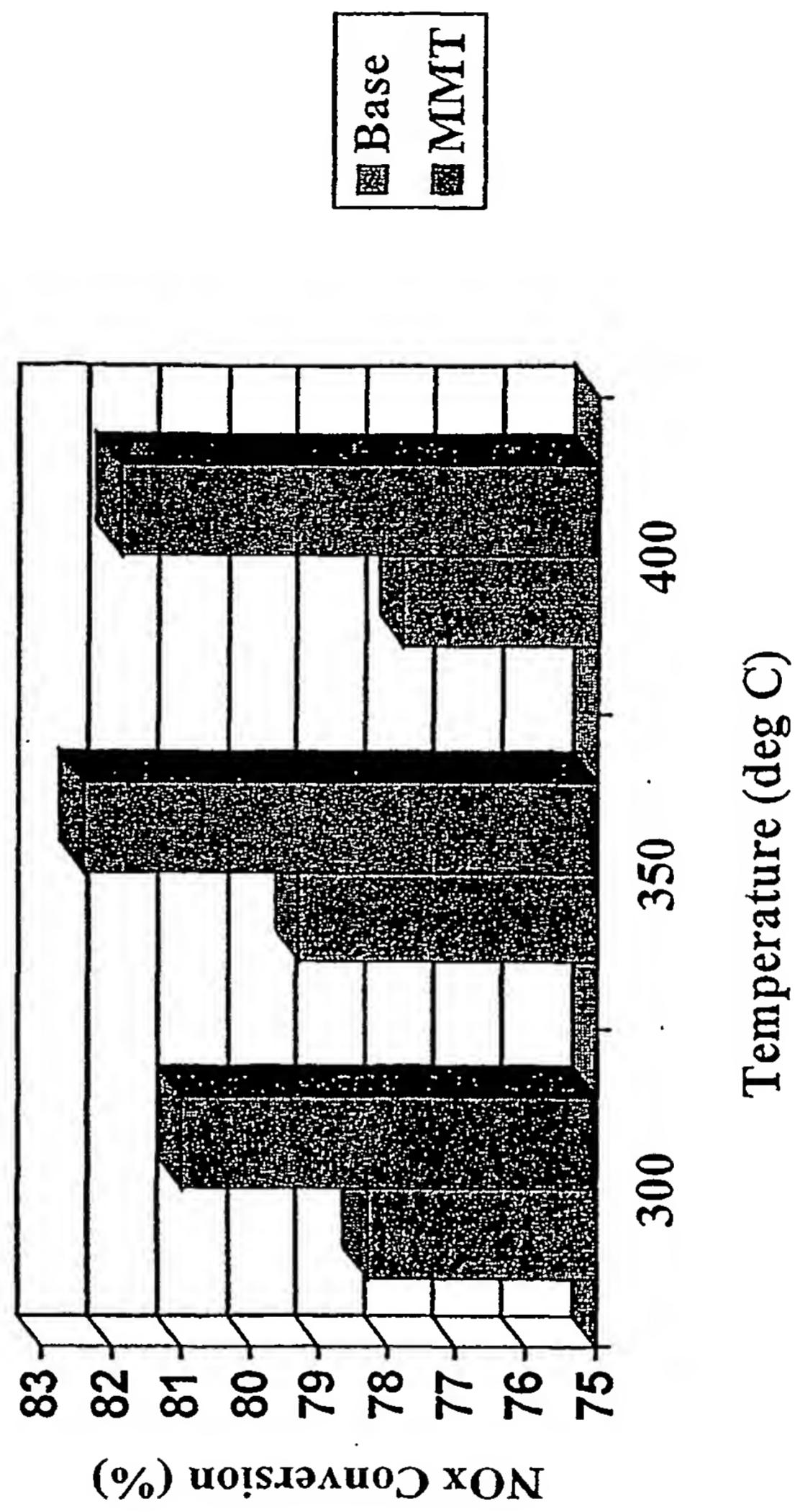
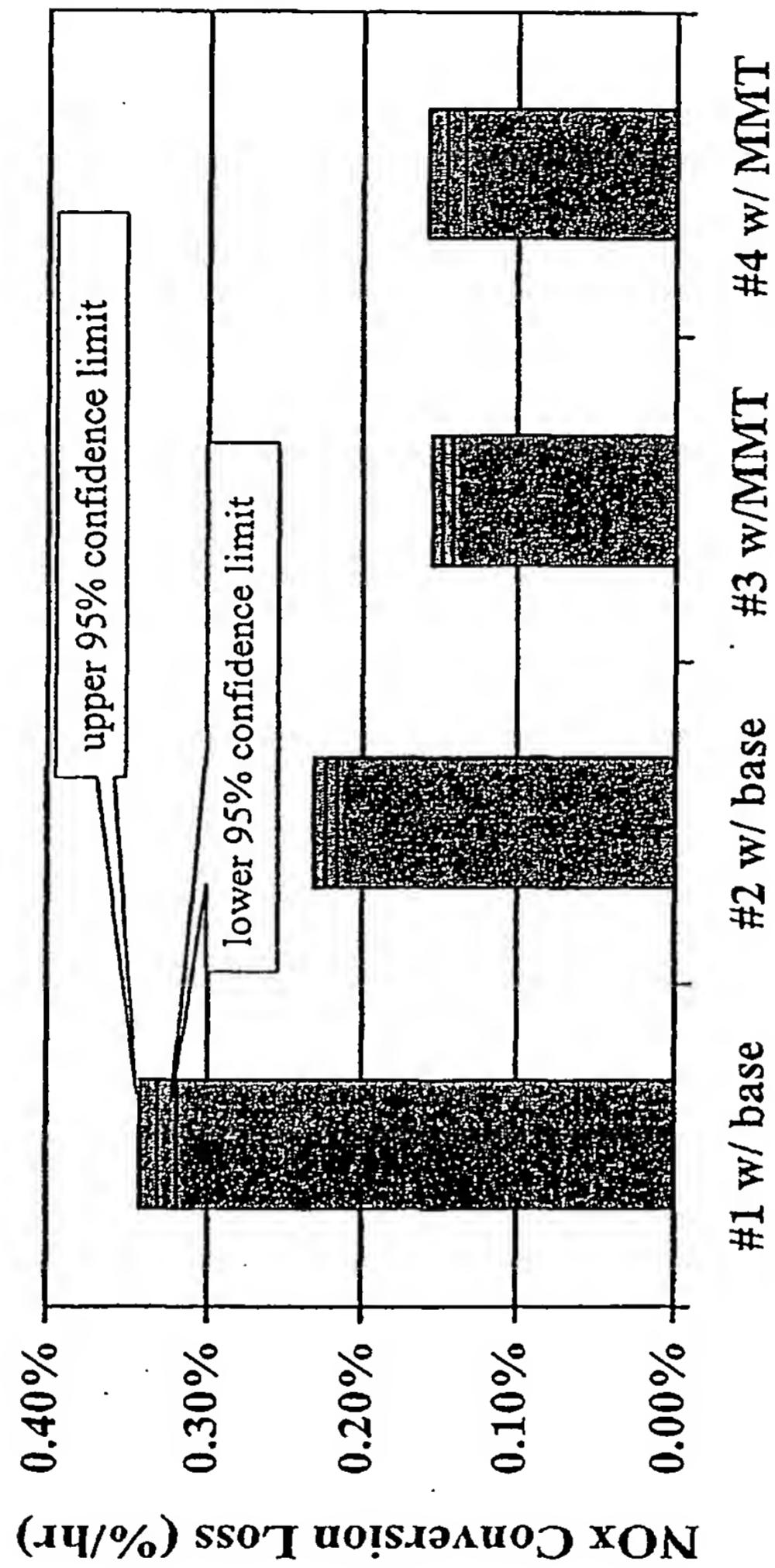


FIGURE 4

NO<sub>x</sub> Conversion Loss With Equivalent  
of 30 ppm Sulfur Fuel



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US01/48863

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :C10L 1/10, 1/32

US CL :44/354; 431/2, 3

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 44/354  
431/2, 3

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	US 6,200,358 B1 (FLEISCHER et al) 13 March 2001, see col. 2, lines 40-67; col. lines 1-26.	1-11, 15- 17, 19-21, 23-28, 30
X	US 5,912,190 A (BARR et al) 15 June 1999, see col. 3, lines 58-67; col. 4, lines 1-67; col. 10-20; claims 1-9.	1-10, 13- 15, 18-21, 24-25, 27, 28, 30
X	US 5,501,714 A (VALENTINE et al) 26 March 1996, see abstract; col. 6, lines 15-56, col. 12, lines 33-41; col. 13, lines 10-16, 66-67; claims 1-14.	1-5, 7-9, 12-14, 16, 27-30
X	US 5,034,020 A (EPPERLY et al) 23 July 1991, see abstract; col. 4, lines 14-59, col. 7, lines 60-68; col. 8, lines 1-61.	1-9, 13-16, 19-21, 25, 27-28

Further documents are listed in the continuation of Box C.  See patent family annex.

• Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
08 MARCH 2002	18 APR 2002

Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer  Cephia D. Toomer
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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/48863

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6,152,972 A (SHUSTOROVICH et al) 28 November 2000; see abstract; col 2, lines 58-67; col 4, lines 1-61; col 5, lines 29-67; col 6, lines 1-38.	1-6, 8, 10- 17, 19-21, 23, 26-28, 30